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PURDUE UNIV LAFAYETTE IND DEPT OF CHEMISTRY
HEAT CAPACITIES OF $H_2O + H_2O_2$ AND $H_2O + N_2H_4$, BINARY SOLUTIONS--ETC(U)
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Report No. N00014-78-C-0035,

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Heat Capacities of $H_2O + H_2O_2^*$, and $H_2O + N_2H_4^*$, Binary Solutions;

Isolation of a Singular Component for C_p of Supercooled Water.

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February 1980

Technical Report, February 1980

Distribution Statement

Prepared for

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

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Purdue Research Foundation
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N00014-78-C-0035 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Heat Capacities of $H_2O + H_2O_2$, and $H_2O + N_2H_4$, Binary Solutions; Isolation of a Singular Component for C_p of Supercooled Water		5. TYPE OF REPORT & PERIOD COVERED Technical Report, Feb. 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. Oguni and C. A. Angell		8. CONTRACT OR GRANT NUMBER(s) N78C0035
9. PERFORMING ORGANIZATION NAME AND ADDRESS Purdue University Department of Chemistry ✓ West Lafayette, IN 47907		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Street Arlington, VA 22217		12. REPORT DATE February 1980
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Division of Sponsored Programs Purdue Research Foundation Purdue University West Lafayette, IN 47907		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) <div style="border: 1px solid black; padding: 5px; text-align: center;"> This document has been approved for public release and sale; its distribution is unlimited. </div>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Intended for publication in the Journal of Chemical Physics.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Water; metastable; supercooled; superheated; heat capacities; anomalies; hydrazine; hydrogen peroxide; homogeneous nucleation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>In an effort to examine further the suggestion that anomalies in the properties of supercooled water reflect the approach to a thermodynamic singularity in the vicinity of $-45^\circ C$, an attempt has been made to separate the total heat capacity of water into "anomalous" and "normal" components. The basis for such a separation used here is extrapolation to zero solute content of C_p of binary aqueous solutions from which the low temperature anomalies have disappeared. We have studied two closely related systems based on the second components</p> <p style="text-align: center;">(cont.)</p>		

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S/N 0102-LF-014-6601

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S/N 0102-LF-014-6601

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Isolation of a Singular Component for C_p of Supercooled Water

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Abstract

In an effort to examine further the suggestion that anomalies in the properties of supercooled water reflect the approach to a thermodynamic singularity in the vicinity of -45°C , an attempt has been made to separate the total heat capacity of water into "anomalous" and "normal" components. The basis for such a separation used here is extrapolation to zero solute content of C_p of binary aqueous solutions from which the low temperature anomalies have disappeared. We have studied two closely related systems based on the second components H_2O_2 and N_2H_4 . The low temperature molar C_p -isotherms are very unusual. The extrapolations to zero solute of C_p isotherms in the two systems yield similar but not identical "normal" components for pure water. The corresponding alternative sets of "anomalous" C_p components vs temperature data, when best-fitted to the singular point equation $C_{p(\text{anom})} = A (T/T_s - 1)^\gamma$, yield within one degree, the same T_s value, 226 K, and exponents either side of the classical value of unity. When the value $\gamma = 1.0$ is assigned to the anomalous components of the dilute aqueous H_2O_2 solutions, the best fit T_s values accurately mirror the behavior of the solution homogeneous nucleation temperatures.

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Introduction

There has been considerable discussion recently of the anomalous temperature dependences of various thermodynamic and relaxational properties of water which become particularly pronounced under supercooled conditions. One interpretation advanced by this laboratory,⁽¹⁻³⁾ and supported by others^(4,5) though by no means generally accepted,⁽⁶⁾ is that the behavior observed reflects approach to a singularity associated with either a liquid state mechanical instability or some internal network singularity. Impeding the proper assessment of this interpretation has been the difficulty of appropriate partitioning of the total observed thermodynamic quantity (C_p , α , κ_T) into normal and singular components, such that the 'critical exponents' can be determined and interpreted.

The purpose of the present measurements has been to provide a plausible basis for performing an appropriate partitioning, for the case of the constant pressure heat capacity. C_p has been chosen for study because it is a quantity which can be measured rapidly for both bulk and emulsion samples, and therefore may be obtained over the maximum possible temperature range.

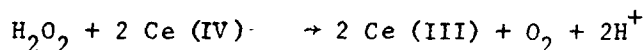
The method of partitioning C_p into normal and anomalous parts which we explore in this paper is based on the extrapolation, to zero solute content, of heat capacity isotherms for binary solutions of water and some appropriate second component which does not exhibit the anomalies characteristic of water. As will be seen, the water anomalies are completely eliminated by addition of some 20% of the second component and, at higher second component-concentrations linear, or approximately linear, composition - C_p functions are found. The latter lend themselves to plausible extrapolations to zero solute content and, from a series of such isotherms, one can thereby obtain a set of C_p vs T points assignable to the "normal" component of the pure water heat capacity.

Some data are already available in the literature⁽⁷⁾ which indicate the form the latter curve may take, but these were obtained from electrolyte solutions which seem in principle less appropriate for the purpose than molecular solutions which preserve much of the liquid-range character of water itself. Our primary choice of system for this study is $H_2O + H_2O_2$ on the basis that each liquid is extensively hydrogen-bonded by oxygen-proton interactions and that the melting points and boiling points of each component are very similar (273.1, 271.5; 373.1, 431.0). The essential difference lies in the proton donor:proton acceptor site ratio, which is 1:1 for water but 1:2 for H_2O_2 . For $H_2O + N_2H_4$ (m.p., 275.0; b.p., 386.7), an almost equally attractive system on which studies are also reported, this ratio is inverted, viz. 2:1. (We note that a 1:1 mixture of H_2O_2 and N_2H_4 would have the same ratio as water and in principle could form a saturated open network which would perhaps exhibit water-like anomalies. Unfortunately hydrazine is as strong a reducing agent as H_2O_2 is an oxidizing agent!) In each case there are composition ranges in which supercooling into the glassy state becomes possible.

Experimental

Materials

Stabilized 50 g% H_2O_2 reagent, which was commercially available from Fisher Chemical Co., was used for the preparation of each aqueous H_2O_2 solution without any purification. The actual concentration was analyzed using the reaction:



with $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ as the standard reagent, and found to be 37.6 mol % H_2O_2 . The fact that no appreciable eutectic phenomena at 217 K and 221 K were observed in the melting curve of the dihydrate, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ ⁽⁸⁾ sample which was prepared on the basis of the analyzed concentration provides a confirmation of the analysis.

N_2H_4 aqueous solutions were prepared using the N_2H_4 reagent from Eastman Kodak Co. without further purification. The presence of some water in the sample was implied by the presence of a small heat absorption at the known $\text{N}_2\text{H}_4 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ eutectic temperature, 218 K. ⁽⁹⁾ This could be used as a basis for quantitative H_2O determination by the simple (but uncommon) method of measuring the eutectic heat absorption as a function of known water additions and extrapolating the linear plot vs weight % H_2O back to zero heat absorption (at negative % added water). The negative addition gives the original water content, 0.6% in this case, with an estimated uncertainty of 0.1 %.

Heat Capacity Measurements

The heat capacities were measured on 5-20 mg samples hermetically sealed in metal pans using the Perkin Elmer DSC-2 instrument with the scanning auto zero accessory. The DSC measured the energy required to keep the temperatures

of sample and reference pans identical during continuous heating or cooling. The heat capacity difference between sample and reference is therefore considered to be proportional to the difference between energies supplied under isothermal conditions on the one hand, and during continuous heating or cooling on the other. This difference is registered as a pen displacement during the run from the 'isothermal hold' position at each temperature, the latter usually being determined from the pen position at beginning and end of each run. The heat capacity of a sample is then derived from the difference between the displacements in scans of empty pan and loaded pan, respectively.

The thermal conditions in the actual measurements on the empty and sample loaded pans, unfortunately, differ slightly depending on time of measurement, different positioning of the pans, environmental conditions and other instrumental factors. These differences have undesirable effects on the display in two ways causing an error in heat capacity determination:

(i) the change of magnitude in displacement Δl , of the pen in the run from the isothermal hold position, and

(ii) the change of isothermal hold pen position without any change of the displacement Δl . Though the former problem is difficult to overcome except by repeating the measurements on the same concentration of samples, the latter may be solved by measuring the isothermal hold position at various temperatures in the range scanned, before and/or after the heating or cooling run. In conventional procedure, one measures the isothermal hold position only at the starting and ending temperatures in a run and assumes those lines at intermediate temperatures to behave in the same manner for the runs of empty and sample-loaded pans. The heat capacity values derived might involve an error of up

to 5% in C_p of 10 mg bulk sample if the factors referred to above are unfavorable. Of course, the smaller the temperature range scanned in one run, the smaller the uncertainty becomes. We therefore measured the isothermal hold displacement at 10 K intervals, scanned the sample over a range of 100 K or so, and introduced the observed 'hold' positions into the data processing.

Both bulk and emulsion samples were used, according to the temperature range studied. Our emulsification procedure followed the method described by Rasmussen and MacKenzie⁽¹⁰⁾ using methyl cyclohexane (MCH) or mixture of MCH and methyl cyclopentane (MCP) as a non-crystallizing carrier.

In the case of emulsions, we measured the heat capacity of the aqueous solution with the same amount of carrier placed in the reference pan as was contained in the sample, i.e. we "offset" the heat capacity due to the carrier. There are some difficulties, in the transfer by microsyringe of emulsion samples, in ensuring that the volume % of water remains identical with the "made up" percentage on which the offset carrier mass is chosen. In three cases, (0.9, 1.67 and 4.15% H_2O_2) the heat capacity of the solution found for the emulsion sample differed from that of the bulk sample of the same nominal composition by as much as 5% - more than the normal uncertainty of the measurement. In these cases the difference was assigned to an offset mismatch, and a constant correction factor applied to the emulsion data. For pure water, new and improved data obtained using both "offset" and "frozen sample comparison" techniques, are being reported elsewhere⁽¹¹⁾ (where they are compared with the behavior of superheated water near the spinodal temperature).

The overall uncertainty in the heat capacities measured for bulk samples is estimated at less than $\pm 2\%$ while, for emulsion samples including the corrections described above, we estimate $\pm 4\%$.

For emulsion samples the runs were terminated by a sudden crystallization presumed to represent approximately the "homogeneous" nucleation temperature for ice I. Bulk samples crystallized at much higher temperatures but these heterogeneous nucleation temperatures also showed systematic composition dependences.

Results

Data in the form C_p vs temperature obtained direct from the experiment are plotted in Fig. 1 for the case of $H_2O + H_2O_2$ solutions of composition 0 - 37% H_2O_2 . The rapid depression of the anomalously increasing low temperature C_p on addition of H_2O_2 is immediately apparent.

From these data, and from similar data for $H_2O + N_2H_4$ solutions, isotherms for the molar heat capacity of the solutions were constructed. These are shown in Figs. 2 and 3. The 240 K ($-33^\circ C$) isotherms must be counted extraordinary by any standard.

The only comparisons which can be made with previous work are with some average heat capacity values between 0 and $26.9^\circ C$ obtained by Giguère et al.⁽¹²⁾ over the whole composition range. These were performed with a Bunsen calorimeter and although an accuracy estimate was not given, comparison with the literature data for pure water indicates the surprisingly high accuracy of 0.1%. Their solution data lie a consistent 2% above ours.

Figures 2 and 3 show extensive binary solution regions above 20% H_2O_2 (or % N_2H_4) in which the composition dependence of C_p is simple, and it is reasonable to suggest that in these regions the molecular species are mixing in a manner appropriate to simple mixtures. Extrapolation of the linear regions to pure

H_2O_2 or pure N_2H_4 heat capacities respectively show the presence of moderate deviations from ideality in each case but not more than expected for simple binary mixtures, i.e. in the "simple" regions the mixtures behave like dispersions of molecules of two liquids which, individually, are similar in character with intermolecular interactions of comparable magnitude. Extrapolations to 0% H_2O_2 or N_2H_4 might therefore be expected to give a heat capacity for H_2O close to that of H_2O molecules interacting in a "normal" liquid state fashion like those of N_2H_4 or H_2O_2 in their pure liquid states. Figures 2 and 3 show, of course, that when H_2O molecules are present in sufficient concentration (> 80%) to permit extensive $\text{H}_2\text{O} - \text{H}_2\text{O}$ interactions, a new and anomalous element enters the heat capacity causing sharp departures from the extrapolated binary C_p isotherm; it is this anomalous element which we wish to separate out.

Using the above-described extrapolations taken to zero H_2O_2 or N_2H_4 contents respectively, we obtain a plot vs temperature of the "normal" component of the H_2O heat capacity. This component, not surprisingly, has a temperature dependence which is similar to those of the > 20 % component 2 binary solutions in each system, some of which may be followed down into the supercooled state to the point of glass formation. Comparisons of these 'normal' components with the actual C_p of pure water on the one hand, and with the 37% binary solutions on the other, are shown in Fig. 4.

Unfortunately for simplicity of interpretation, the 'normal' component for H_2O is not independent of the binary system used to extract it. That obtained from the $\text{N}_2\text{H}_4 + \text{H}_2\text{O}$ system is some 10% lower and corresponds closely with that derived from a recently reported study of heat capacities in binary salt + water solutions.⁽⁷⁾ A similar plot ~ 2% higher is obtained if the appropriate binary solution behavior in the "simple mixture" region for $\text{N}_2\text{H}_4 + \text{H}_2\text{O}$ solutions is taken to be curved as the data suggest rather than linear. It is not clear which, if either, of the $\text{H}_2\text{O}_2 - \text{H}_2\text{O}$ based and $\text{N}_2\text{H}_4 - \text{H}_2\text{O}$ based

"normal" components is to be preferred. Indeed, it could be argued that because the lone pair/proton ratios in H_2O_2 and N_2H_4 are inverted, and both different from that of water, neither system extrapolation is appropriate and that a mean value should be chosen. We will use both in the following analysis. It has not escaped our attention that hydroxylamine NH_2OH (m.p., 306.2; b.p., 329.7) has the same lone pair/proton ratio as water.

The glass transition phenomena seen at 140 K (the same temperature observed for vapor deposited vitreous water by McMillan and Los by DTA measurements at comparable scan rates⁽¹³⁾) will be examined in more detail in a separate publication.

Discussion

We can now proceed to the main objectives of this work. In Fig. 5 we show the anomalous components of the heat capacity of water obtained as the difference of the total C_p and the 'normal' component based on the $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ solution data extrapolation. Also shown are plots of the anomalous part of the heat capacities of several binary $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ solutions based on a "normal" components taken from the extrapolated C_p vs % H_2O_2 lines of Fig. 2 at the appropriate compositions. Except for the case of pure H_2O the lines through the points are sight-guides for clarity only. For pure water the solid line is the plot of the singular point equation⁽²⁾

$$C_{p(\text{anomalous})} = A \left(\frac{T}{T_s} - 1 \right)^{-\gamma} \quad (1)$$

with parameters $T_s = 224.9$, $\gamma = 1.34$, $A = 0.922$, these being the values which give the best fit to the data points. A log-log plot of these data with slope $\gamma = 1.34$ is shown in Fig. 6a. We will return to the remaining plots in Fig. 6 in a moment.

In Fig. 7 we show a similar log-log plot for the "anomalous" component of $C_p(\text{H}_2\text{O})$ based on the subtraction, from the total C_p , of a H_2O and solution "normal" component obtained from the curvilinearly extrapolated $\text{H}_2\text{O} + \text{N}_2\text{H}_4$ isotherms of Fig. 3. For this estimate of the "normal" component for pure water, the best fit parameters to Eq. (1) are $T_s = 226.4$ K, $\gamma = 0.933$ and $A = 2.309$. The fit is very good as indicated by a R value of 0.9996. If the "normal" component based on the linear extrapolation of binary solution data is used, Fig. 3, dashed line, an even better fit of the anomalous or excess C_p to Eq. (1) is obtained, $R = 0.9998$, with $T_s = 225.2$ and γ unchanged at 0.933. We note that this latter T_s value is almost identical with the best fit value for $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ - based excess C_p data, but that γ is now a little less than unity. A value of unity is anticipated from a mean field theory for the anomalous fluctuations near a singular point when T is near T_s , or when higher order terms are weakly contributing.⁽¹⁴⁾ Fig. 7(b) shows that the fit of the data to Eq. (1) with $\gamma = 1.0$ is also excellent.

It can be seen from the above that an intermediate "normal" component, possibly to be obtained from study of $\text{H}_2\text{O} + \text{NH}_2\text{OH}$ solutions, would yield anomalous C_p values conforming well to mean field theory expectations, with a singular temperature slightly below the value of 228 K (-45°C) thought previously to be the best value.⁽²⁾ This suggests the relevance of a Landau-type theory such as described recently by Alexander and McTague for crystallization of simple fluids with weakly first order fluid-crystal transitions.⁽¹⁵⁾

Although our primary aim in this work was to establish the feasibility of a mean-field description of the anomalous thermodynamic behavior of supercooled water, we are also interested in possible parallels between the manner in which this behavior is affected by small amounts of 2nd components and the way it is affected by pressure. The latter effect was reported recently for the case of isothermal compressibility⁽¹⁶⁾ but without the benefit of any separation of anomalous from normal components.

The anomalous components of the heat capacities of the dilute $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ solutions are subjected to best fit log-log plots in Fig. 6a. They do not show a very coherent pattern of behavior. On the other hand, if we assign γ in Eq. (1) the value of unity suggested by mean field theory for singular point heat capacities, we obtain, as constrained best fits, the plots in Fig. 6b. In this case, although the individual fits are poor, the pattern of parameters is more intelligible since A varies systematically with % H_2O_2 , and T_s closely follows the line of homogeneous nucleation temperatures for the binary solutions. The latter relation is shown in Fig. 8 which summarizes equilibrium and non-equilibrium phase relation data for this system. T_s' is the best fit value, and rapidly approaches zero.

There is a clear parallel between these findings and those of the earlier observation, from compressibility measurements, of the effect of pressure on $T_s^{(16)}$. The latter was found to follow T_H in its pressure dependence when γ was held constant at the appropriate value for the low pressure data. In those measurements, however, there was no satisfactory basis for separating anomalous from normal components of the property (compressibility) under study. From the present measurements it now seems that, when the water structure is severely disrupted by intrusion of molecules of a second component, the system does not conform well to Eq. (1), though the parallel of T_s and T_H when the constraint $\gamma = 1.0$ is introduced in the fitting procedure suggests it has some memory of it. Evidently the correlations involved in the cooperative phenomenon can grow in but only to a limited extent, thus eliminating the singular behavior at lower temperatures. The same may well be the case for high pressure behavior studied over the maximum temperature range.

It is significant that the parameter A of Eq. (1), obtained from Fig. 6(b) (see inset) tends linearly to zero at about 12% H_2O_2 (Fig. 6, inset) where little anomalous character remains in the total C_p . The value of A should reflect the fraction of water molecules in the system taking part in the cooperative behavior. In the high pressure study, A for κ_T remained almost constant while T_S decreased parallel with T_H . The different behavior seen in the present case no doubt reflects the fact that water molecules are becoming increasingly "tied down" in non-cooperative structures with increasing H_2O_2 content. Concomitantly the character of the cooperative water molecule associations must change from one of a three-dimensionally connected gel-like structure⁽¹⁷⁻¹⁹⁾ to one of small unconnected clusters ('sol' structure). The increasingly poor fits to Eq. (1) at higher concentrations may reflect the loss of gel-like character, where the "gel" is to be interpreted in the special sense of gelation of four bonded, hence open-structured, water molecules as described recently by Stanley.⁽¹⁹⁾

Concluding Remarks

The attitude one takes to the present findings is largely a matter of taste and prejudice. On the one hand, one could conclude immediately from the fact that attempts to isolate a unique anomalous component of C_p are less than completely successful, (Fig. 4) that attempts to interpret the behavior of water in these terms are futile. On the other hand, one could argue that a unique separation by the binary solution method could not be expected, and that the fact that a background term intermediate between the two values extrapolated gives mean field behavior for the anomalous component, makes the analysis of water properties in these terms highly plausible.

Our view is that this sort of judgement is to be deferred pending results of similar solution studies currently being performed for the properties, compressibility and expansivity.

Acknowledgements

It is a pleasure to acknowledge support of this research by the Office of Naval Research under Contract No. N00014-78-C-0035.

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Figure Captions

- Figure 1 Heat capacities of water and $\text{H}_2\text{O} + \text{D}_2\text{O}$ solutions as functions of temperature. Lower portion gives detail on low H_2O_2 content behavior. Open symbols represent bulk sample data; closed symbols represent emulsion sample data.
- Figure 2 Heat capacity isotherms for $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ solutions obtained from data plots displayed in Fig. 1.
- Figure 3 Heat capacity isotherms for $\text{H}_2\text{O} + \text{N}_2\text{H}_4$ solutions obtained as for Fig. 2. (No emulsion samples studied in this system.)
- Figure 4 "Normal" component of the heat capacity of water assessed by extrapolation to zero solute content of data of Figs. 2 and 3. Also shown for comparison are plots of the total C_p 's of pure water and the 37% solutions. The latter are glass-forming. Low temperature data in these cases were obtained during reheating runs and exhibit the normal relaxational 'overshoot' of the glass transition phenomenon.
- Figure 5 Anomalous components of the heat capacity of H_2O and $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ solutions obtained by subtraction of Fig. 4 background from Fig. 1 total C_p data. The curve passing through the points for pure water is the best fit of Eq. (4) to the data.
- Figure 6 Log-log plots for anomalous components of C_p of H_2O and $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ solutions, based on Eq. (4). Upper portion; best fit representations. Lower portion; best fits of data subject to constraint of constant exponent value, viz. $\gamma = 1.0$. Inset: composition dependence of A parameter of Eq. (4) for constrained best fits.

Figure 7 Log-log plot for anomalous component of H_2O obtained using 'normal' component derived from $N_2H_4 - H_2O$ solution data, see Figs. 3 and 4.

Figure 8 Phase diagram for $H_2O + H_2O_2$ system showing heterogeneous and homogeneous nucleation temperatures, and T_g values based on both constrained (T_g) and unconstrained (T_g') fits to the anomalous contributions to solution C_p 's. Glass transition temperatures, where measurable, are also shown.

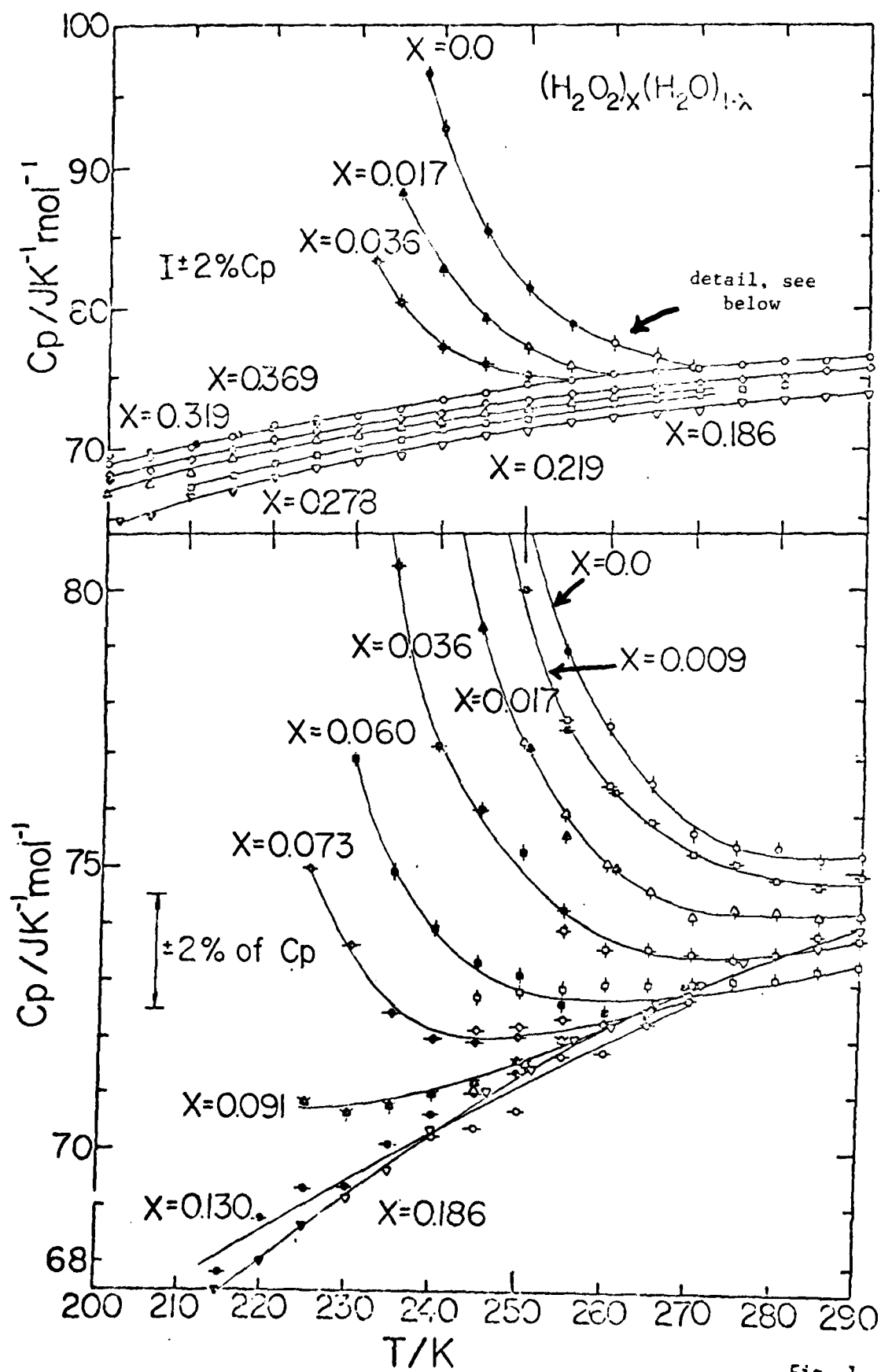


Fig. 1

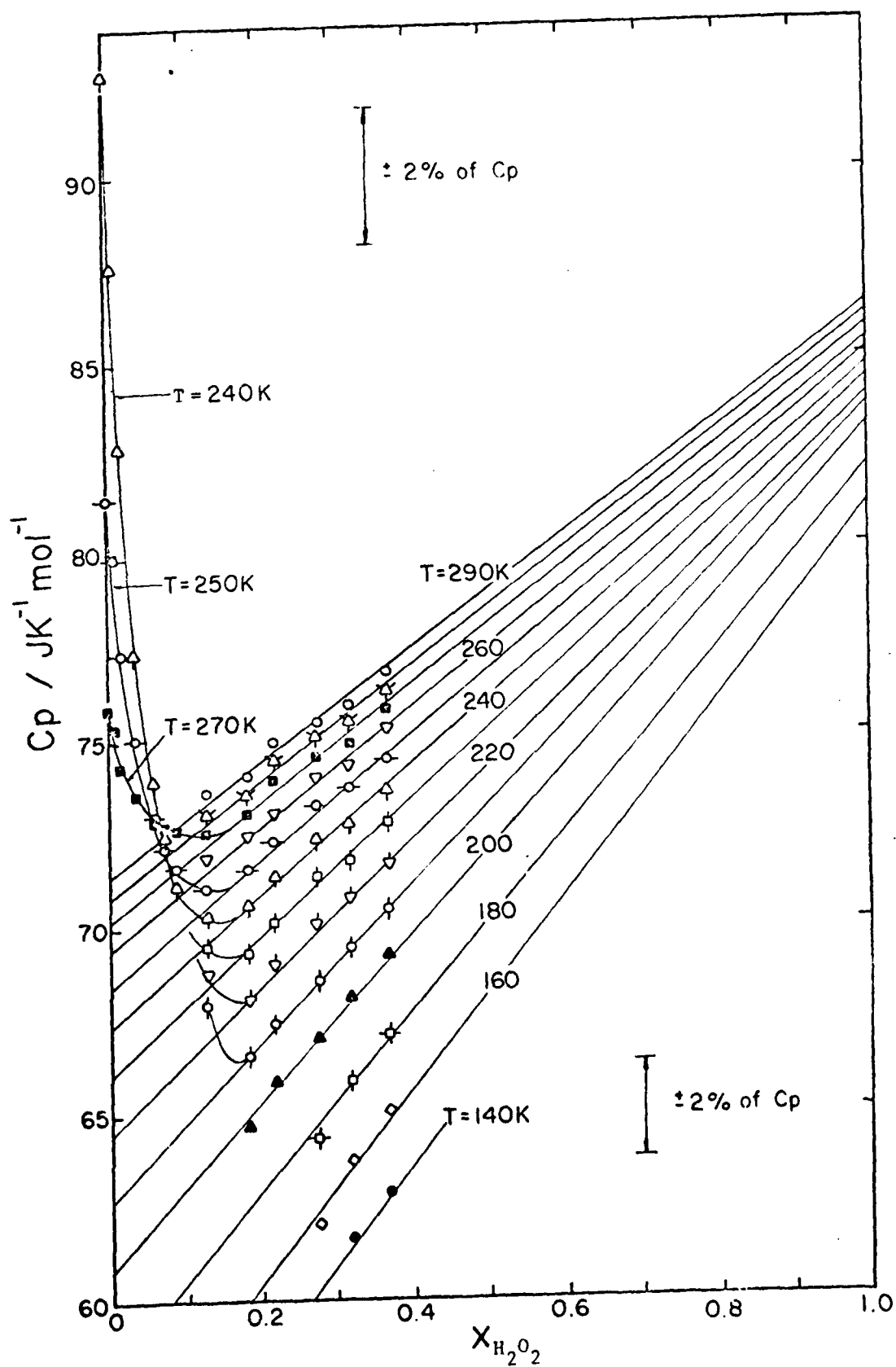


Fig. 2

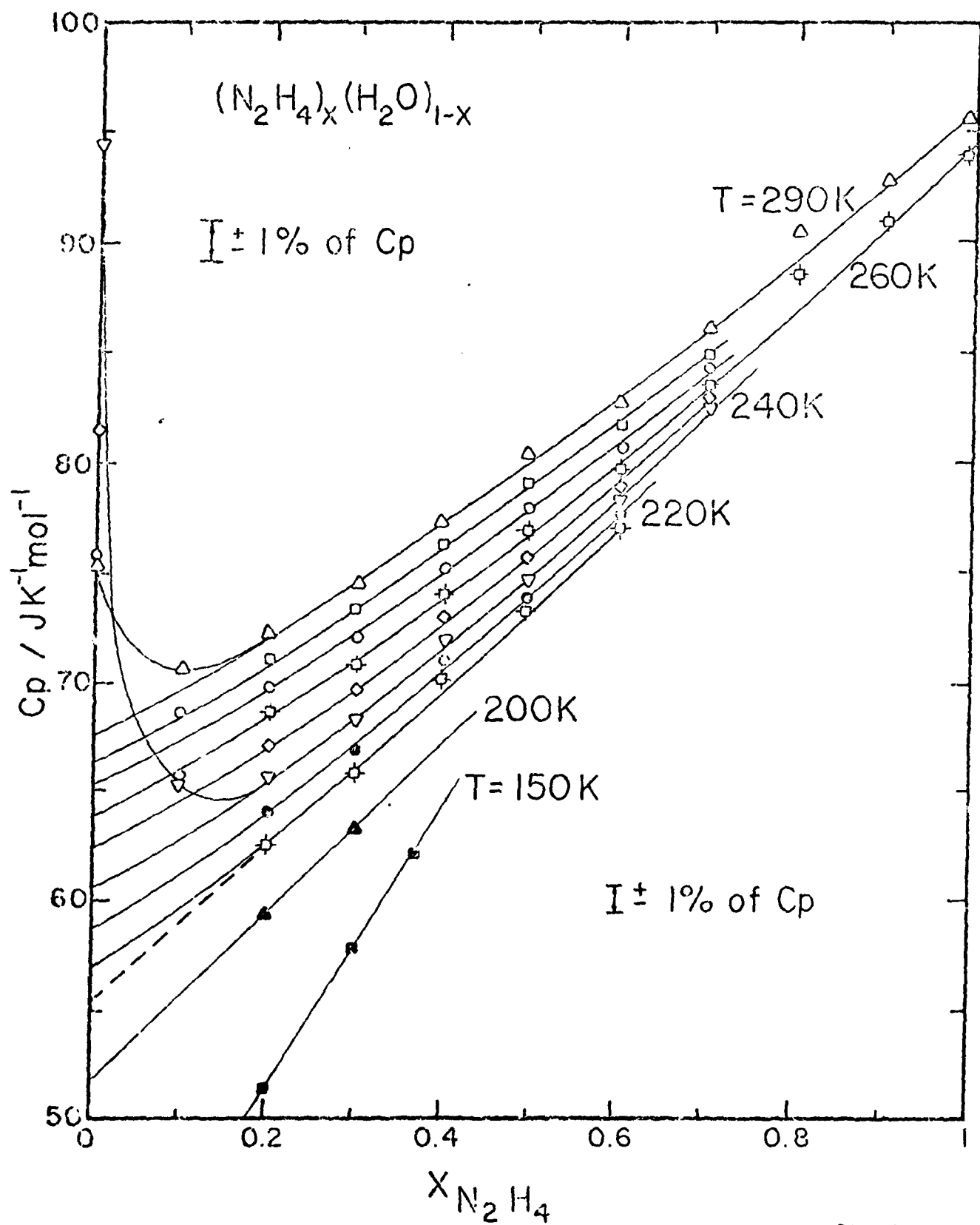


Fig. 3

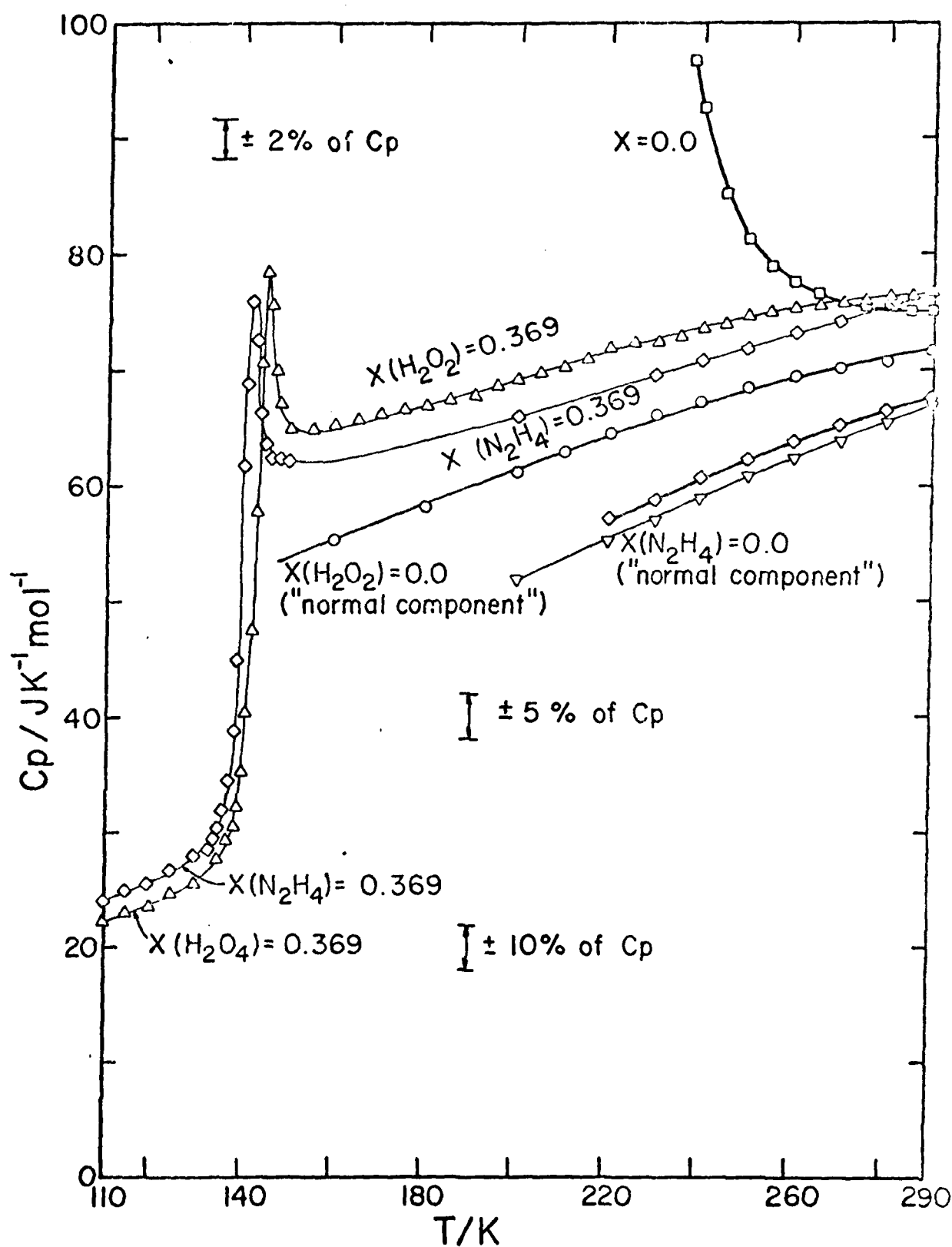


Fig. 4

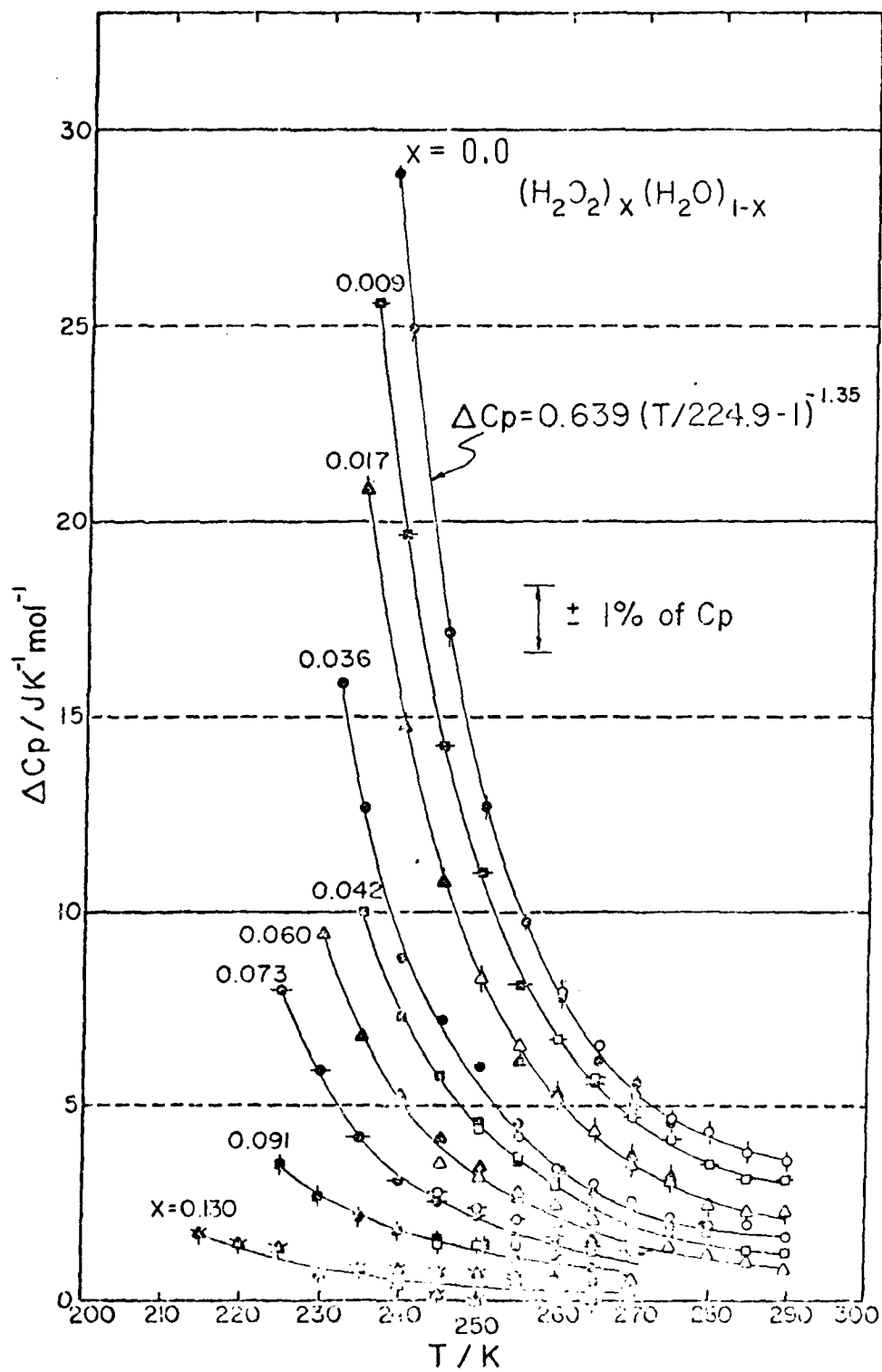


Fig. 5

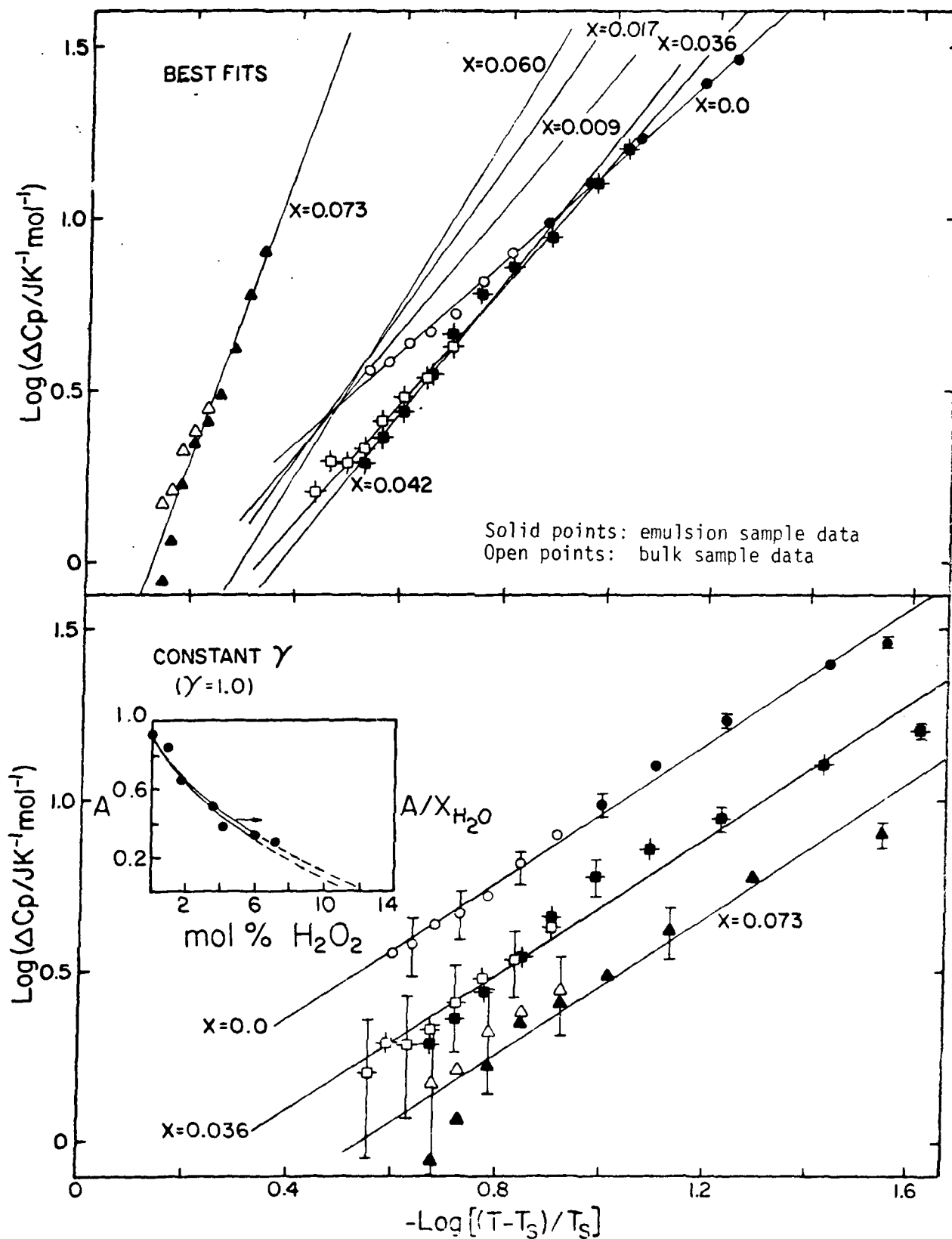


Fig. 6

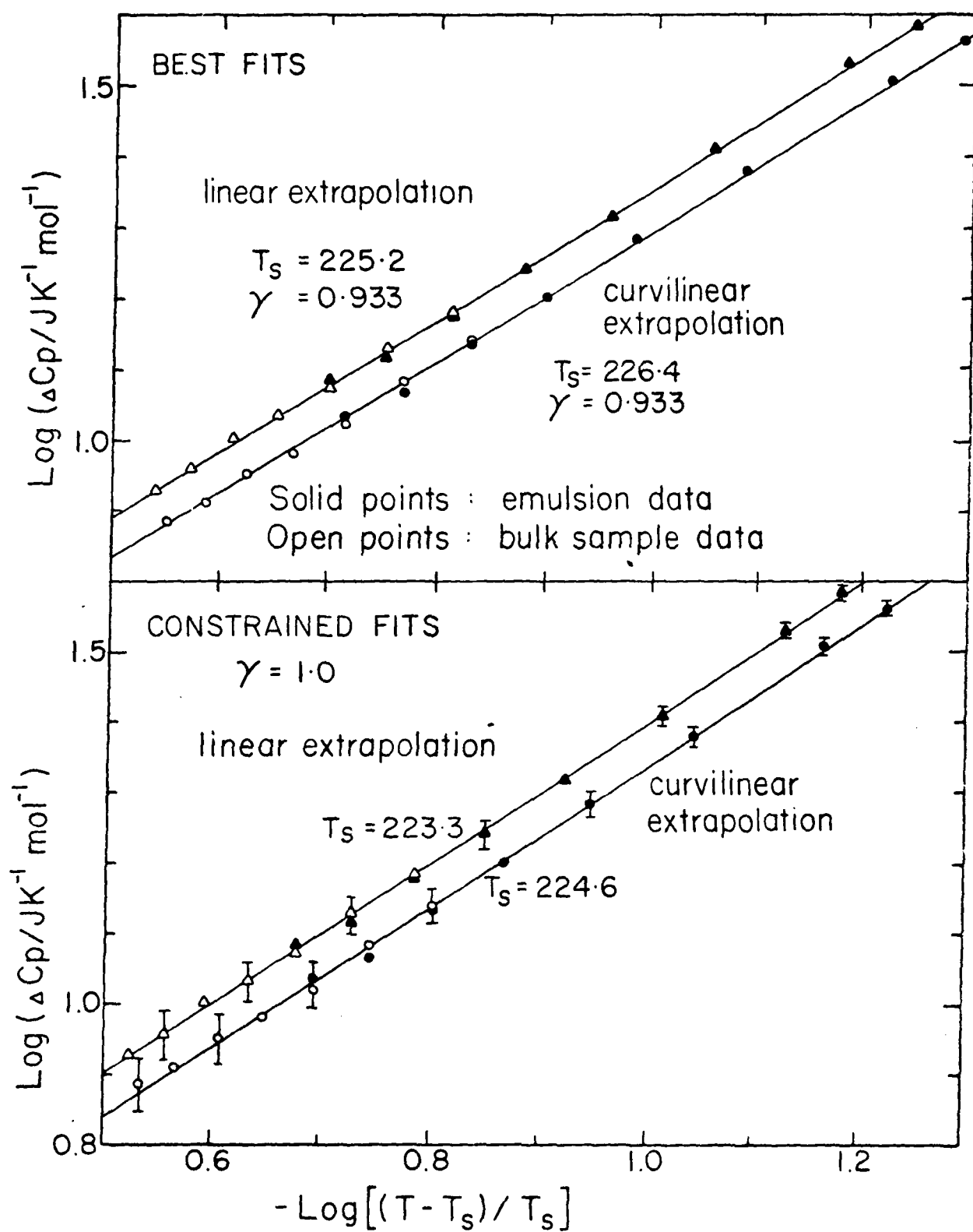


Fig. 7

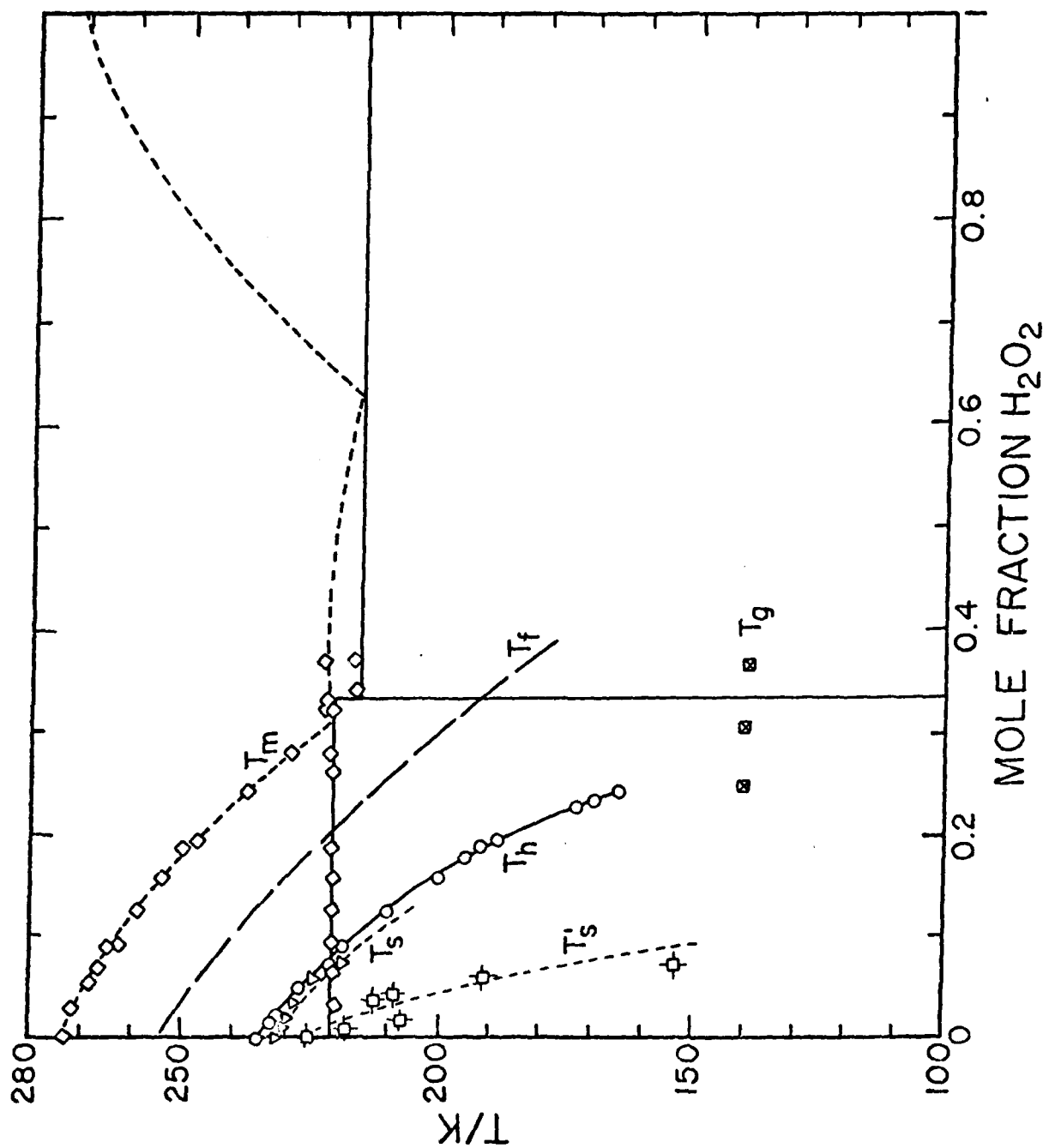


Fig. 8

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